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Notes:

1. Untranslatable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as it is.

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FULL CONTENTS

[Claim(s)]

[Claim 1] The high-density Pt system metal content metal conductivity oxide which adds the compound containing at least a kind of metal of 12 to periodic table 15 group, or this metal to eight to periodic table 10 group's Pt system metal oxide, or the metal conductivity oxide containing this Pt system metal and alkaline-earth metals, sinters, and is characterized by things.

[Claim 2] The high-density Pt system metal content conductivity oxide according to claim 1 characterized by the loadings of the compound containing said periodic table 12 - 15 group metal, or this metal being 0.001-0.5mol.

[Claim 3] Add the compound containing at least a kind of metal of 12 to periodic table 15 group, or this metal to eight to periodic table 10 group's Pt system metal oxide, or the metal conductivity oxide containing this Pt system metal and alkaline-earth metals, and it sinters to it. The manufacture procedure of the high-density Pt system metal content metal conductivity oxide characterized by obtaining a high-density sintered compact.

[Claim 4] The compound containing said periodic table 12 - 15 group metal An oxide, the carbonate, a nitrate, Sulfate, hydroxide, a chloride, the fluoride, a sulfide, or an iodide, Or the manufacture procedure of the high-density Pt system metal content metal conductivity oxide according to claim 3 which are those mixtures and is characterized by obtaining the high-density sintered compact of 65% or more of relative density by adding these 0.001-0.5mol of compounds.

[Claim 5] As a compound containing at least a kind of metal or this metal of said 14 to periodic table 15 group Adding a lead or a lead compound, Bi, or Bi compound is added, Or the manufacture procedure of the high-density Pt system metal content metal conductivity oxide according to claim 3 or 4 characterized by to add what mixed a lead or a lead compound, Bi, or Bi compound, or adding what mixed a lead compound, Bi compound, and other metallic compounds.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to high-density periodic table octavus - a high-density 10 group Pt system metal oxide, the high-density metal conductivity oxide containing this Pt system metal and alkaline-earth metals, and its manufacture procedure. This high-density oxide is useful as a target for

electrode material pellicle.

[0002]

[Description of the Prior Art] Development of memories using the pellicle of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PTZ, $0 < x \leq 1$) or $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) which is dielectric material, such as DRAM and FRAM, is performed briskly. The general mechanism of this dielectric membrane memory is shown in drawing 1. By a dielectric membrane memory, especially, membranous fatigue characteristics and a membranous data-hold trait are important, and a film with little deterioration is being developed by the device of material or the forming-membranes method. Development of the material of the electrode (Pt electrode) 3 in the mechanism shown in drawing 1 is observed as technology which holds especially a key. This electrode 3 is formed on SiO_2 prepared on the lamina basalis (p-Si) 1, and a part predetermined in the electrode 3 is covered with the ferroelectric membrane 4 (for example, PZT, SBT, etc.). Although the method using Pt electrode as electrode was common until now It was reported that ferroelectric membrane carries out hydrogen deterioration according to the catalytic effect of Pt (Y. Shimamoto, KKushida-Abdelghafar, H. Miki and Y.Fujisaki, Appl.Phys.Lett., 70, 1997, 3096).

[0003] Then, search of the electrode material which replaces Pt was performed briskly, and promising ** of the use of a good oxide material (IrO_2 , RuO_2 , SrRuO_3 , CaRuO_3 , SrIrO_3) of matching with an oxide dielectric was carried out. As the electrode which consists of such oxide material was used instead of Pt electrode or it was shown in drawing 1, the layer of the metal conductivity oxide electrode 5 was prepared on the ferroelectric membrane 4, and the procedure of laminating Pt electrode 3' on it further was proposed as an effective procedure of preventing deterioration of a dielectric trait. It can be said that the resistivity of the bulk is below 10^{-5} (300K) $\Omega\cdot\text{m}$, and especially the oxide (SrRuO_3 , CaRuO_3 , SrIrO_3 grade) material containing the periodic table 8 - 10 group Pt system metal, and alkaline-earth metals is an outstanding electrode material. It is becoming a well-known fact that the deterioration preventive effect of a dielectric memory trait of the pellicle which consists of this metal conductivity oxide is high. However, as performance of a memory, it was not still satisfactory, and the homogeneity of the pellicle of SrRuO_3 grade, surface morphology, etc. are bad, and have left the room for an improvement. It is raised that the density of the target of SrRuO_3 grade used by the sputtering method is dramatically low as the main cause.

[0004] The metal conductivity oxide containing the periodic table 8 - 10 group Pt system metal, and alkaline-earth metals mixed the carbonate, nitrate, or oxide which contains alkaline-earth metals or alkaline-earth metals in Pt system metal or Pt system metal oxide, and was heat-treated and compounded in the air or oxygen environment. Although there is also the procedure of carrying out direct sintering from metal, in order to carry out dilation in the stage where an oxide is formed by this procedure, sintering, after compounding an oxide is common. The powder of the oxide ABO_3 ($\text{A}=\text{Sr, Ca, Ba}; \text{B}=\text{Pt, Ir, Ru, Rh}$;) was also compounded by the same procedure. For example, at 1000-1200 degrees C, carry out weighing of Ru and SrCO_3 by the molar ratio of 1:1, carry out ball mill mixture through ethanol, after desiccation, carry out temporary quenching for 0.5 to 3 hours, grind, carry out compression moulding of the obtained powder, and subsequently The acquired Plastic solid was set in the furnace, it sintered at 1000-1350 degrees C for 0.5 to 6 hours, and the object had been obtained. Thus, about obtained SrRuO_3 , change of the relative density to sintering temperature is shown in drawing 2.

Relative density shall show the relative value of the real density at the time of making theoretical density $\rho_0 = 6.47$ (g/cm^3) of SrRuO_3 into 100% here. Even if it sintered at which temperature so that clearly from drawing 2, the relative density of the obtained sintered compact was lower than 65%. Although

sintered at 1250 degrees C, a SEM image is shown in drawing 3 . Drawing 3 shows that grain growth is hardly seen and sintering is not advancing. Thus, grain growth does not happen easily and the thing whose relative density of the obtained sintered compact is very low is because the degree of sintering is very bad. The dissociation pressure of RuO₂ is shown in drawing 4 as reference (Kozo Tanabe, Tetsuro Shimizu, Kazuo Fueki, a metal oxide and a multiple oxide, Kodansha, the 284th page). With usual Ceramics Sub-Division, the amount of volatilization of Ru oxide (RuO₃, RuO₄) will increase, and this oxide will cause a density fall conversely, so that sintering temperature becomes high to density going up, so that sintering temperature becomes high.

[0005] As described above, it was dramatically difficult to obtain the high-density sintered compact of the metal conductivity oxide containing the periodic table 8 - 10 group Pt system metal, and alkaline-earth metals. Then, development of the procedure of raising the density of the metal conductivity oxide of SrRuO₃ grade was desired.

[0006]

[Problem to be solved by the invention] According to the conventional metal oxide manufacture procedure which was described above, the relative density of the periodic table 8 obtained - a 10 group Pt system metal oxide, or the metal conductivity oxide containing this Pt system metal and alkaline-earth metals was lower than about 65%, and the sintered compact which has the relative density beyond this was not able to be obtained. The crack and the chip took place easily at the time of operation, and injection power was not raised in the target which consists of oxide material with low density, but time was further required at the time of the vacuum suction of weld slag equipment, and it had the problem that mass-production nature was low. Then, this invention makes it a technical problem for 65% or more of relative density to offer the periodic table 8 - the 10 group Pt system metal oxide which have 70% or more preferably, the metal conductivity oxide containing this Pt system metal and alkaline-earth metals, and its manufacture procedure.

[0007]

[Means for solving problem] Pt system metal content metal conductivity oxide of this invention adds the compound containing at least a kind of metal of 12 to periodic table 15 group, or this metal to eight to periodic table 10 group's Pt system metal oxide, or the metal conductivity oxide containing this Pt system metal and alkaline-earth metals, and sinters to it. Difficult Pt system metal oxide material of obtaining a high-density sintered compact according to this invention, [or the powder of the metal conductivity oxide electrode material containing this Pt system metal and alkaline-earth metals] The compound containing the periodic table 12 - 15 group metal, or this metal the specified quantity, usual [0.001-0.5mol of], and when 0.03-0.05mol 0.01-0.07mol adds still more preferably preferably A sintering trait is improved and a high-density metal conductivity oxide electrode material may be manufactured easily. [the loadings of the compound containing this periodic table 12 - 15 group metal, or this metal] If it is less than 0.001mol, the relative density of the sintered compact obtained will become low, and there is a problem of not being desirable in using as a target for sputtering. Moreover, when it exceeds 0.5mol, by adding many addition ingredients to the metal conductivity oxide which is the main ingredients, the generated amount of a different-species compound increases and there is a problem of spoiling conductivity.

[0008] [the target for sputtering used in order to form conventionally the electrode material which consists of the periodic table 8 - a 10 group Pt system metal oxide, or conductive metallic oxide containing Pt system metal and alkaline-earth metals] It was obtained by the procedure of sintering

without an assistant, and the relative density of the sintered compact was lower than about 65%. [these metal oxides] by carrying out specified quantity addition of the compounds, such as metal of 12 to periodic table 15 group of a low-melt point point, or its oxide (for example, ZnO, PbO, Bi₂O₃, SnO₂, Tl₂O₃, In₂O₃ grade) Grain growth is carried out at low temperature, volatilization of a volatilization component is controlled and eburnation advances, and since high-density Pt system metal oxide or the high-density metal conductivity oxide containing Pt system metal and alkaline-earth metals is obtained, it becomes possible to obtain the electrode material which consists of this high-density oxide. An improvement of the membranous adhesion strength at the time of becoming a lamination film and the diffusion deterrent effect to the electrode material of a dielectric component (Pb of PZT, Bi of SBT) are also expectable by dielectric membrane material being included in an electrode material. Therefore, finally it can contribute to manufacture of a highly efficient memory.

[0009]

[Mode for carrying out the invention] The periodic tables 8 - 10 group Pt system metal which are used by this invention are Ru, Rh, Pd, Os, Ir, and Pt, and are Ru, Rh, Ir, and Pt preferably. Alkaline-earth metals are Ca, Sr, and Ba. SrRuO₃, SrIrO₃, CaRuO₃, BaRuO₃, Sr₂RuO₄, Sr₂IrO₄, Ba_{0.67}Sr_{0.33}IrO₃ grade, and its mixture are contained in a metal conductivity oxide, for example. The periodic table 12 group metal used by this invention is zinc, cadmium, and the mercury, are zinc preferably, and [13 group metal] It is B, aluminum, Ga, In, and Tl, and is In and Tl preferably, 14 group metal is C, Si, germanium, and Sn and Pb, and it is Sn and Pb preferably, and 15 group metal is N, P, As, Sb, and Bi, and is Bi preferably. As a compound containing at least one sort of such metal An oxide, the carbonate, a nitrate, sulfate, hydroxide, a chloride, the fluoride, a sulfide, Or an iodide or its mixture can be used. For example, PbO, Pb₂O, Pb₃O₄, Pb₂O₃, BiO, Bi₂O₃, Bi₂O₅, SnO₂, Tl₂O₃, In₂O₃, ZnO, PbCO₃ -- three -- Pb(NO₃)₂ -- three -- Bi(NO₃)₃ -- three -- PbSO₄ -- four -- Bi(OH)₃ -- three -- PbCl₂ -- two -- PbCl₄ -- four -- SnCl₄ -- four -- BiCl₃ -- three -- PbF₂ -- two -- [TlF and] TlF₃, BiS, Bi₂S₃, TlS, In₂S, PbI₂ grade, or its mixture is desirable.

[0010] By adding a Pb compound like Pb or Pb oxide as said periodic table 14 group metal An electrode material suitable for combination with the dielectric material of PbTiO₃ which can be made to contain Pb in a high-density sintered compact electrode material, and contains Pb, Pb(Zr, Ti) O₃, and O(Zr (Pb, La), Ti)₃ grade can be obtained. By adding a Bi compound like Bi or Bi oxide as a periodic table 15 group metal SrBi₂Ta₂O₉ which can be made to contain Bi in a high-density sintered compact electrode material, and contains Bi, and an electrode material suitable for combination with Bi stratified compound dielectric material of SrBi₂TaNbO₉ grade can be obtained. Moreover, by adding what mixed a lead or a lead compound, Bi, or Bi compound by the desired ratio PbBi₂Nb₂O₉ which can be made to contain Bi and Pb in a high-density sintered compact electrode material, and contains Bi and Pb, and an electrode material suitable for combination with Bi stratified compound dielectric material of PbBi₂TaNbO₉ grade can be obtained. A thing suitable for combination with the dielectric material which can be made to contain Bi, Pb, and other elements in a high-density sintered compact electrode material, and contains the element of Bi, Pb, and others can be obtained by adding further again what mixed a lead compound, Bi compound, and other metallic compounds.

[0011] Pt system metal content metal conductivity oxide of this invention is obtained like the procedure of conventional technology of manufacturing the above-mentioned oxide ABO₃. for example, the carbonate, nitrate, or oxide containing Pt system metal and alkaline-earth metals -- almost -- equimolar -- [a ratio / weighing is carried out and] Carry out ball mill mixture through organic solvents, such as

ethanol, and temporary quenching is carried out at about 1000-1200 degrees C after desiccation for about 0.5 to 3 hours. On the same conditions as usual, add the compound which grinds and contains the periodic table 12 - 15 group metal, or this metal in the obtained powder, carry out ball mill mixture through organic solvents, such as ethanol, carry out compression moulding, and subsequently An object can be obtained by setting the acquired Plastic solid in a furnace and sintering at about 1000-1350 degrees C for about 0.5 to 6 hours.

[0012]

[Working example] The example of this invention is hereafter explained with reference to Drawings. (Example 1) 0.02-0.10mol of Bi(s) $2O_3$ were added to IrO_2 powder, and ball mill mixture was carried out through ethanol. Compression moulding was carried out on condition of 0.5 - 1.0 ton/cm² after desiccation, and the acquired Plastic solid was sintered at 1000-1300 degrees C for 0.5 to 6.0 hours. The sintered compact was obtained similarly [for not adding Bi $2O_3$] as control. Change of the relative density to $2OBi_3$ loadings of IrO_2 obtained sintered compact is shown in drawing 5 . The theoretical density of IrO_2 is 11.65g/cm³. It turns out that it can check that relative density improves to 65% or more, and 72% or more of IrO_2 sintered compact is also obtained for relative density by adding Bi $2O_3$ from drawing 5 . The SEM image of IrO_2 sintered compact which does not add Bi $2O_3$, and the IrO_2 sintered-compact fracture surface which added 0.05mol of Bi(s) $2O_3$ is shown in drawing 6 and 7, respectively. If drawing 6 is compared with drawing 7 , it is clear by adding Bi $2O_3$ that change is clearly looked at by the crystal grain diameter, and sintering is advancing. Thus, IrO_2 thin film electrode with little deterioration with uniform sufficient surface morphology was obtained using the target for sputtering which consists of an obtained high-density sintered compact. Moreover, the resistivity of this pellicle was 1.5×10^{-6} ohm-m about Bi $2O_3$ at the time of 0.05mol addition.

[0013] (Example 2) Weighing of Ru and $SrCO_3$ was carried out by the molar ratio of 1:1, and ball mill mixture was carried out through ethanol. After desiccation, at 1000-1200 degrees C, temporary quenching was carried out for 1 hour, and it ground. 0.01-0.06mol PbO was added to the obtained temporary-quenching powder, ball mill mixture was carried out, compression moulding was carried out on condition of 0.5 - 1.0 ton/cm², and the acquired Plastic solid was sintered at 1000-1350 degrees C for 0.5 to 6 hours. The sintered compact was obtained similarly [for not adding PbO] as control. Change of the relative density to the PbO loadings of $SrRuO_3$ obtained sintered compact is shown in drawing 8 . It turns out that it can check that relative density improves to 65% or more, and 80% or more of $SrRuO_3$ is also obtained for relative density by adding PbO from drawing 8 . The SEM image of the 0.06mol PbO addition $SrRuO_3$ sintered-compact fracture surface is shown in drawing 9 . If drawing 3 is compared with drawing 9 , it is clear by adding PbO that change is clearly looked at by the crystal grain diameter, and sintering is advancing. Thus, $SrRuO_3$ thin film electrode with little deterioration with uniform sufficient surface morphology was obtained using the target for sputtering which consists of an obtained high-density sintered compact. Moreover, the resistivity of this pellicle was 6.0×10^{-6} ohm-m about PbO at the time of 0.06mol addition.

[0014] (Example 3) Weighing of Ru and $SrCO_3$ was carried out by the molar ratio of 1:1, and ball mill mixture was carried out through ethanol. After desiccation, at 1000-1200 degrees C, temporary quenching was carried out for 0.5 to 3 hours, and it ground. 0.01-0.06mol Bi $2O_3$ was added to the obtained $SrRuO_3$ temporary-quenching powder, ball mill mixture was carried out, compression moulding was carried out on condition of 0.5 - 1.0 ton/cm², and the acquired Plastic solid was sintered

at 1000-1350 degrees C for 0.5 to 6 hours. The sintered compact was obtained similarly for not adding Bi₂O₃ as control. Change of the relative density to 2OBi₃ loadings of SrRuO₃ obtained sintered compact is shown in drawing 10 . It turns out that it can check that relative density improves to 65% or more, and 85% or more of SrRuO₃ is also obtained for relative density by adding Bi₂O₃ from drawing 10 . The SEM image of the 0.06mol Bi₂O₃ addition SrRuO₃ sintered-compact fracture surface is shown in drawing 11 . If drawing 3 is compared with drawing 11 , it is clear by adding Bi₂O₃ that change is clearly looked at by the crystal grain diameter, and sintering is advancing. Thus, SrRuO₃ thin film electrode with little deterioration with uniform sufficient surface morphology was obtained using the target for sputtering which consists of an obtained high-density sintered compact. Moreover, the resistivity of this pellicle was 3.0×10^{-6} ohm-m about Bi₂O₃ at the time of 0.06mol addition.

[0015] (Example 4) In an example 2, when the procedure of an example 2 is repeated except for having used PbO and Bi₂O₃ instead of PbO, the same result is obtained.

(Example 5) In examples 2 and 3, the loadings of PbO and Bi₂O₃ was 0.1-0.5mol, and the procedure of the example 2 was repeated. Change of the relative density of the obtained sintered compact is shown in drawing 12 and drawing 13 . Also in this loadings, improvement in the relative density by excipients has been checked.

[0016] Although Pb oxide and Bi oxide were used as Ru, Ir, and an alkaline-earth-metals content compound as a Pt system metal in the above-mentioned example as Sr carbonate, the periodic table 12 - 15 group metal content compound Even if it uses the other above-mentioned Pt system metal, an alkaline-earth-metals content compound and the periodic table 12 - 15 group metal, and its compound, the target for sputtering which a high-density sintered compact is obtained similarly and consists of this sintered compact is useful although the desired oxide film electrode is obtained.

[0017]

[Effect of the Invention] According to this invention, the metal conductivity oxide electrode material with which the sintering trait has been improved and which has high density is offered by carrying out specified quantity addition and sintering 12 to periodic table 115 group's metal, or its compound to the oxide containing the periodic table 8 - 10 group Pt system metal. By using this electrode material, the desired oxide electrode is obtained and, finally quality improvement of a dielectric membrane memory device, mass-production nature, and highly efficient-ization are attained.

[Brief Description of the Drawings]

[Drawing 1] The typical sectional view showing the cross-sectional mechanism of the conventional general ferroelectric random-access memory.

[Drawing 2] Graph which shows change of the relative density to the additive-free sintering temperature of SrRuO₃.

[Drawing 3] The photograph in which the SEM image of the additive-free SrRuO₃ sintered-compact fracture surface is shown.

[Drawing 4] Graph which shows change of the dissociation pressure to the temperature of RuO₂.

[Drawing 5] Graph which shows change of the relative density of IrO₂ sintered compact to 2OBi₃ loadings.

[Drawing 6] The photograph in which the SEM image of the additive-free IrO₂ sintered-compact fracture surface is shown.

[Drawing 7] The photograph in which the SEM image of the 0.05mol Bi₂O₃ addition IrO₂ sintered-compact fracture surface is shown.

[Drawing 8] Graph which shows change of the relative density of SrRuO₃ sintered compact to PbO loadings.

[Drawing 9] The photograph in which the SEM image of the 0.06mol PbO addition SrRuO₃ sintered-compact fracture surface is shown.

[Drawing 10] Graph which shows change of the relative density of SrRuO₃ sintered compact to 2OBi₃ loadings.

[Drawing 11] The photograph in which the SEM image of the 0.06mol Bi₂O₃ addition SrRuO₃ sintered-compact fracture surface is shown.

[Drawing 12] Graph which shows change of the relative density of SrRuO₃ sintered compact to high concentration PbO loadings.

[Drawing 13] Graph which shows change of the relative density of SrRuO₃ sintered compact to 2Ohigh concentration Bi₃ loadings.

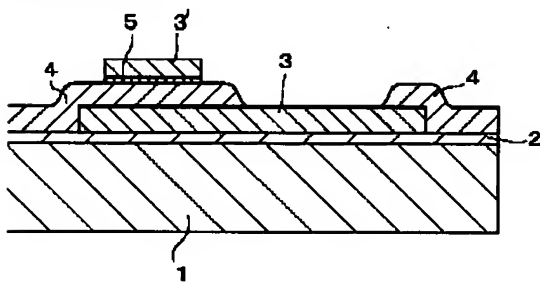
[Explanations of letters or numerals]

1 Lamina Basalis (P-Si) 2 SiO₂

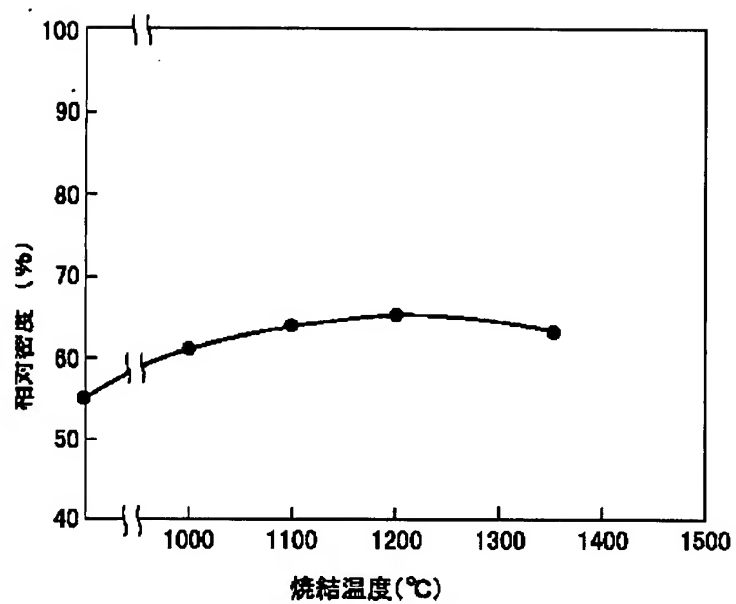
3 Electrode (Pt Electrode) 4 Ferroelectric Films (PZT, SBT, Etc.)

5 Metal Conductivity Oxide Electrode

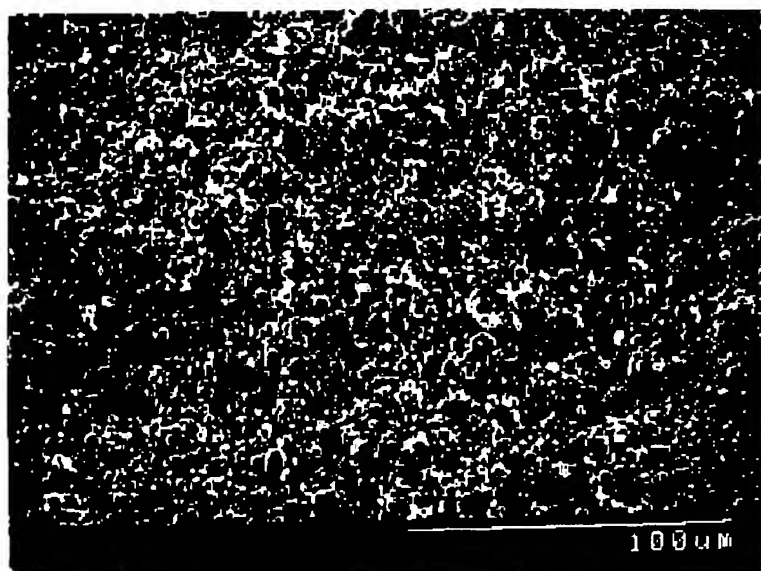
[Drawing 1]



[Drawing 2]

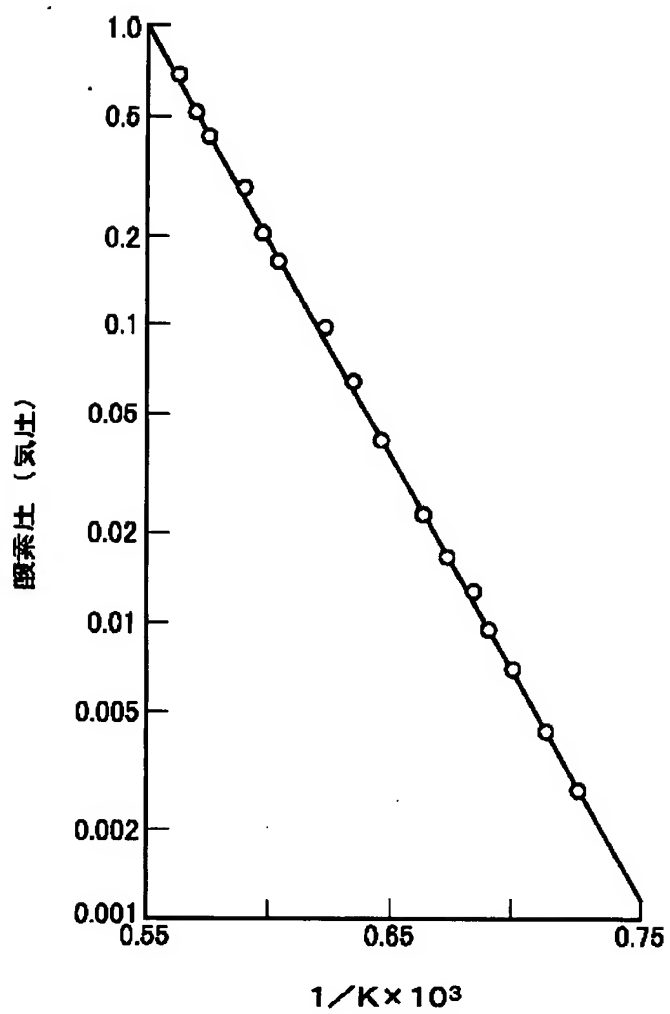


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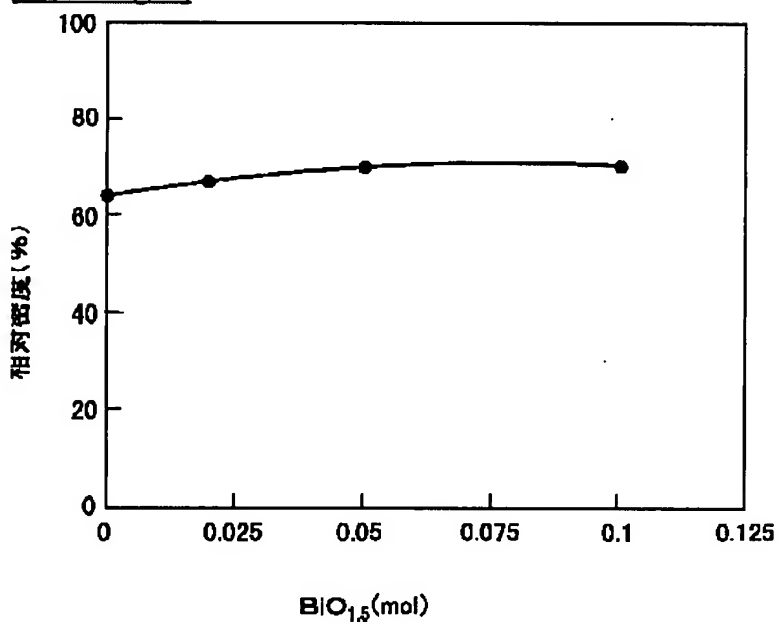


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[Drawing 4]

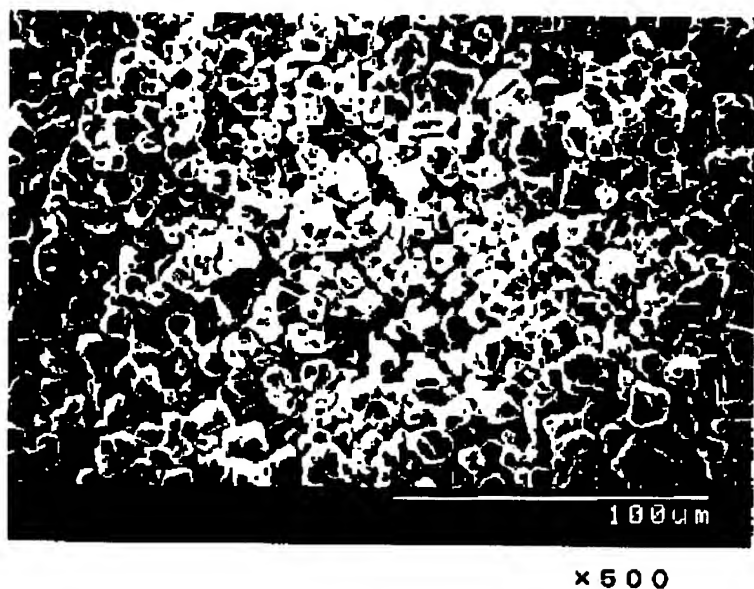


[Drawing 5]

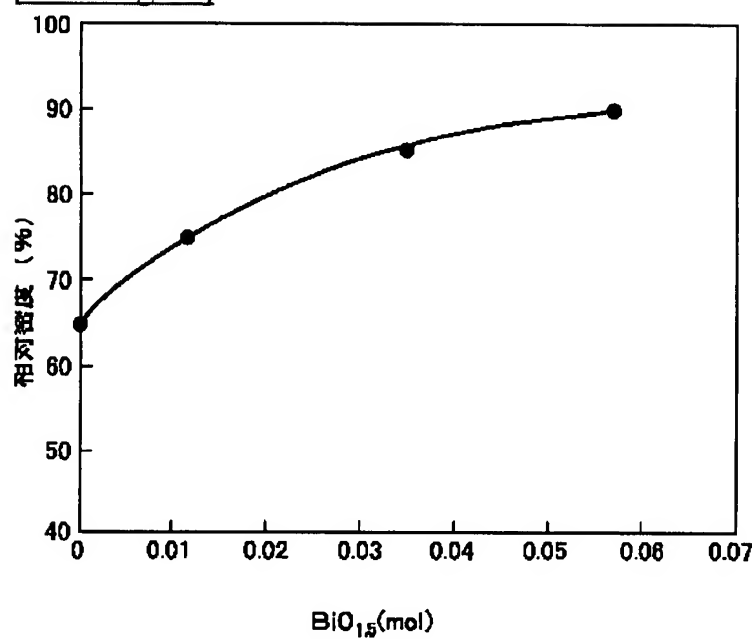


[Drawing 6]

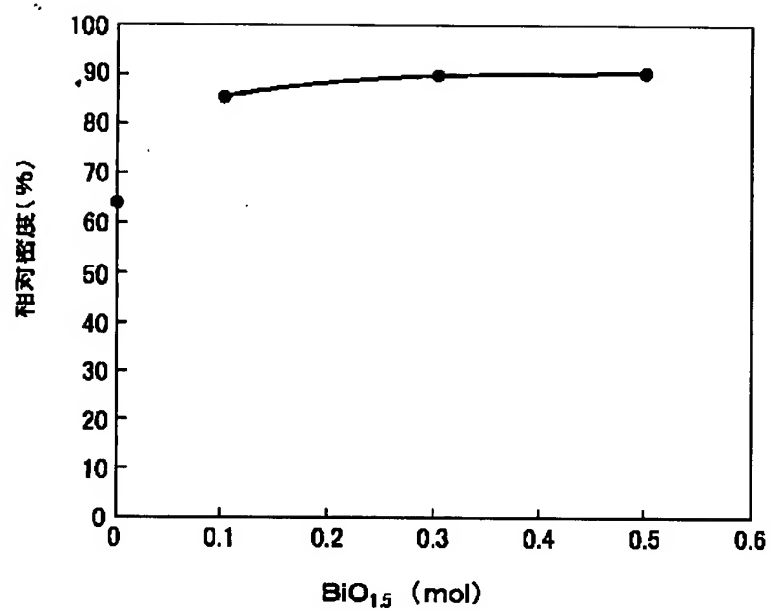
[Drawing 9]



[Drawing 10]



[Drawing 11]



[Translation done.]